

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 101 812 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

23.05.2001 Bulletin 2001/21

(51) Int. Cl.⁷: **C10G 1/10**, C10J 3/46,
B09B 3/00

(21) Application number: 99926929.3

(86) International application number:
PCT/JP99/03612

(22) Date of filing: 05.07.1999

(87) International publication number:
WO 00/02977 (20.01.2000 Gazette 2000/03)

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

(30) Priority: 08.07.1998 JP 19285998

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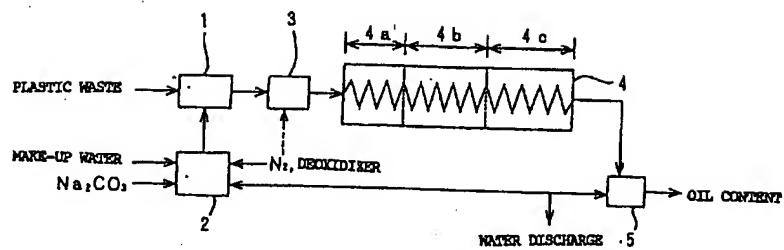
(54) **METHOD FOR CONVERTING CHLORINE-CONTAINING WASTE PLASTIC TO OIL**

(57) There is provided an oilification process for chlorine-based plastic waste characterized in that a mixture of plastic waste including chlorine-based plastic and an aqueous solution containing carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal or several kinds of these compounds, in which the concentration of dissolved oxygen is controlled so as to be not higher than 0.5 mg/liter, is heated; chlorine in the plastic waste is released during a process of transfer to a supercritical condition and/or under a supercritical condition; and the plastic waste is decomposed, or characterized in that an aqueous solution containing carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal or several kinds of these compounds is heated; melted plastic waste including chlorine-based plastic is mixed in the aqueous solution

during a process of transfer to a supercritical condition and/or under a supercritical condition; the concentration of dissolved oxygen in the aqueous solution is controlled so as to be not higher than 0.5 mg/liter before or during the mixing of the plastic waste; chlorine in the plastic waste mixed in the aqueous solution is released; and the plastic waste is decomposed.

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FIG. 1



Description

TECHNICAL FIELD

- 5 [0001] The present invention relates to an oilification process for chlorine-based plastic waste using supercritical water.

BACKGROUND ART

- 10 [0002] Conventionally, as a method for reusing plastic waste, an attempt has been made to recover useful oily matters by decomposing plastic waste (oilification treatment) by using supercritical water. -
- [0003] However, in the case where plastic waste is chlorine-based plastic, chlorine ions are released from plastic waste when oilification is effected using supercritical water. These chlorine ions cause heavy corrosion of stainless-steel-based metals, which is used for an oilification apparatus. Specifically, because oilification using supercritical water
- 15 is effected under high temperatures and high pressures, pitting, crevice corrosion, stress corrosion cracking, and other defects caused by chlorine ions occur in the stainless-steel-based metal. The degree of corrosion differs depending on the composition of stainless steel and the concentration of released chlorine ion.
- [0004] On the other hand, a study has been made to use nickel-based alloys, which have special chemical composition and are invulnerable to corrosion, as a material for oilification apparatus. However, the nickel-based alloys are
- 20 expensive, and greatly increase the construction cost of apparatus.
- [0005] For the above-described reasons, for example, a process has been developed in which plastic waste is thermally decomposed at temperatures of 300 to 350°C in a dechlorination apparatus, and after chlorine is removed, the plastic waste is introduced into an oilification apparatus made of stainless steel, which is less costly than nickel-based alloys, to effect oilification by using supercritical water. In this case, however, comparing with the case of direct oilifica-
- 25 tion, the process is complicated, and the number of equipments constituting the apparatus increases. Therefore, the construction cost of the whole oilification facility is very high.

DISCLOSURE OF THE INVENTION

- 30 [0006] The present invention has been made in view of such a situation, and accordingly an object thereof is to provide an oilification process for chlorine-based plastic waste, in which an apparatus using an inexpensive stainless-steel-based metal can be employed, and the number of equipments is small.
- [0007] The oilification process for chlorine-based plastic waste in accordance with the present invention is characterized in that a mixture of plastic waste including chlorine-based plastic and aqueous solution containing carbonate of
- 35 an alkali metal or hydroxide or carbonate of an alkali earth metal or several kinds of these compounds, in which the concentration of dissolved oxygen is controlled so as to be not higher than 0.5 mg/liter, is heated; chlorine in the plastic waste is released during a process of transfer to a supercritical condition and/or under a supercritical condition; and the plastic waste is decomposed.
- [0008] Also, an oilification process for chlorine-based plastic waste in accordance with another mode of the present invention is characterized in that aqueous solution containing carbonate of an alkali metal or hydroxide or carbonate of
- 40 an alkali earth metal or several kinds of these compounds is heated; melted plastic waste including chlorine-based plastic is mixed in the aqueous solution during a process of transfer to a supercritical condition and/or under a supercritical condition; the concentration of dissolved oxygen in the aqueous solution is controlled so as to be not higher than 0.5 mg/liter before or during the mixing of the plastic waste; chlorine in the plastic waste mixed in the aqueous solution is
- 45 released; and the plastic waste is decomposed.
- [0009] Also, in the oilification process for chlorine-based plastic waste in accordance with the present invention, chlorine released from the plastic waste can be neutralized by carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal.
- [0010] Also, in the oilification process for chlorine-based plastic waste in accordance with the present invention, as
- 50 means for controlling the concentration of dissolved oxygen, nitrogen gas can be blown or a deoxidizer can be added.
- [0011] Also, in the oilification process for chlorine-based plastic waste in accordance with the present invention, as the deoxidizer, sodium sulfite, sodium nitrite, or hydrazine can be used.

BRIEF DESCRIPTION OF THE DRAWINGS

- 55 [0012]

FIG. 1 a flow diagram showing chlorine-based plastic waste treatment process in accordance with a first example

of the present invention; and

FIG. 2 a flow diagram showing chlorine-based plastic waste treatment process in accordance with a second example of the present invention.

5 BEST MODE FOR CARRYING OUT THE INVENTION

[0013] Chlorine-based plastic waste to be treated by the oilification process in accordance with the present invention may be any kind of plastic containing chlorine. For example, vinyl chloride resin, polyvinylidene chloride, polychlorotrifluoroethylene, and the like can be cited. Also, it may be plastic waste other than chlorine-based one, for example,

10 a mixture with polyethylene, polypropylene, polystyrene, and the like.

[0014] Before undergoing treatment, the chlorine-based plastic waste is ground into powder. The size of powder is preferably not larger than 2 mm in diameter when the powder is assumed to be a sphere having the same volume. If the powder is too large, when the pulverized plastic waste is supplied to an oilification apparatus after being mixed with aqueous solution, it may become incapable of being supplied smoothly, and also the efficiency of oilification treatment

15 decreases.

[0015] Next, the pulverized plastic waste, having a dissolved oxygen concentration of 0.5 mg/liter or lower, is mixed with aqueous solution containing carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal.

[0016] The control of dissolved oxygen concentration may be accomplished after the preparation of the mixed liquid. Specifically, after the pulverized plastic waste is mixed with aqueous solution containing carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal to yield a mixed liquid, the mixed liquid may be treated so that the concentration of dissolved oxygen in the mixed liquid is not higher than 0.5 mg/liter.

[0017] As a means for making the concentration of dissolved oxygen in the aqueous solution or mixed liquid not higher than 0.5mg/liter, for example, blowing of nitrogen gas and addition of a deoxidizer can be cited. As the deoxidizer, for example, sodium sulfite, sodium nitrite, and hydrazine can be used. These deoxidizers may be used singly or in combination of two or more kinds.

25 [0018] By making the dissolved oxygen concentration not higher than 0.5 mg/liter, corrosion reaction (cathode reaction) under the supercritical condition can be restrained.

[0019] The aqueous solution mixed with chlorine-based plastic waste contains one or more kinds selected from carbonate of an alkali metal, hydroxide of an alkali earth metal, and carbonate of an alkali earth metal. As examples of these components, sodium carbonate, calcium carbonate, magnesium hydroxide, calcium hydroxide, and the like can be cited.

30 [0020] The amount of addition of carbonate or hydroxide should be not higher than the equivalent of total quantity of released chlorine at the later-described subcritical portion and supercritical portion, and preferably should be 1.1 to 1.2 equivalents.

35 [0021] Here, the reason for using these salts and the like will be explained.

[0022] When chlorine-based plastic waste is heated at a temperature of 300°C and higher, chloride is released. The released chloride dissolves in water into hydrochloric acid, which heavily corrodes metallic materials excluding special metallic materials. To prevent such corrosion caused by hydrochloric acid, it is thought to neutralize the hydrochloric acid with sodium hydroxide, for example. When sodium hydroxide is used, however, the remaining sodium hydroxide causes heavy corrosion and stress corrosion cracking in a short period of time. In the present invention, corrosion can be prevented by using sodium carbonate etc. without the use of hydroxide of an alkali metal.

40 [0023] In this description, a subcritical condition is defined as a condition of a temperature of 250 to 350°C and a pressure of 25 to 30 MPa. Also, a portion under a subcritical condition in an oilification apparatus is referred to as a subcritical portion. Similarly, in this description, a supercritical condition is defined as a condition of a temperature of 350 to 550°C and a pressure of 25 to 30 MPa. Also, a portion under a supercritical condition in an oilification apparatus is referred to as a supercritical portion.

45 [0024] From the chloride-based plastic waste in the adjusted mixed liquid, chloride is released under the subcritical condition, and the released chloride (hydrochloric acid) is immediately neutralized by salt or hydroxide in the mixed liquid. Therefore, in the subsequent treatment under the supercritical condition, no hydrochloric acid is present in the mixed liquid, so that an inside wall of the apparatus is not corroded by hydrochloric acid. Also, even if salt etc. having not been used for neutralization under the subcritical condition remains in large quantities in the mixed liquid and enters the supercritical portion, the mixed liquid under the supercritical condition does not become strongly alkaline, resulting in no occurrence of corrosion, because hydroxide of an alkali metal is not used.

50 [0025] For the mixed liquid from which chlorine is released under the subcritical condition, the plastic waste in the mixed liquid is next decomposed into oil content and gas content under the supercritical condition. The obtained oil content and gas content can be used as fuel and the like.

55 [0026] Even under the supercritical condition, the chloride remaining in the plastic waste is released. The released chloride (hydrochloric acid) is immediately neutralized by salt or hydroxide in the mixed liquid.

[0027] In the above explanation, the mixed liquid of plastic waste and aqueous water has been transferred from the subcritical condition to the supercritical condition. However, the waste plastic may be mixed in the aqueous solution after the aqueous solution is changed from the subcritical condition to the supercritical condition.

[0028] Also, for thermoplastic plastic, plastic waste melted by the application of heat may be mixed in the aqueous solution. The mixing may be performed during a process of transfer to the supercritical condition, or may be performed under the supercritical condition.

[0029] Next, examples of the embodiment of the present invention will be described with reference to the accompanying drawings.

10 First example

[0030] In FIG. 1, plastic waste is supplied into a mixer 1, and is mixed with aqueous solution supplied from a tank 2, turning to slurry. The aqueous solution supplied from the tank 2 contains carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal, and is adjusted by nitrogen gas (N_2) or a deoxidizer so that the dissolved oxygen concentration is not higher than 0.5 mg/liter.

[0031] The control of dissolved oxygen concentration by using nitrogen gas or a deoxidizer may be accomplished in the mixer 1 or on the downstream side thereof.

[0032] The slurry in the mixer 1 is introduced into an oilification apparatus 4 by a slurry feeder 3. In the oilification apparatus 4, the slurry is first preheated at a preheating portion 4a, and then chloride contained in the plastic waste in the slurry is released at a subcritical portion 4b. The released chlorine is neutralized by carbonate or hydroxide in the slurry. Thereafter, the slurry moves into a supercritical portion 4b, where the plastic waste in the slurry is decomposed.

[0033] After the decomposition, the slurry is discharged from the oilification apparatus, and is separated into oil content and water content by an oil separator 5. Some of the separated water content is discharged to the outside of the system, and the remainder thereof is supplied into the tank 2. To the tank 2, in addition to the water content supplied from the oilification apparatus 4, makeup water and sodium carbonate, in this example, are supplied from the outside of the system. Thereby, the quantity of aqueous solution sent to the mixer 1 and the concentration of sodium carbonate are kept constant.

Second example

[0034] FIG. 2 shows another example of embodiment of the oilification process for chlorine-based plastic waste in accordance with the present invention. In FIG. 2, the same reference numerals are applied to the same elements as those in FIG. 1, and the duplicated explanation is omitted.

[0035] Thermoplastic plastic is melted by a melter 21 provided with a motor as a driving means, and is mixed in aqueous solution in which the dissolved oxygen concentration is controlled so as to be not higher than 0.5 mg/liter during a process of transfer to the supercritical condition or under the supercritical condition of the oilification apparatus.

Working examples

40 Working examples 1 to 6

[0036] Plastic waste having a composition given in Table 1 was oilified by the apparatus shown in FIG. 1.

[0037] The aqueous solution in the tank 2 was adjusted by the blowing of nitrogen gas and the addition of sodium sulfite so that the dissolved oxygen concentration is 0.1 to 0.5 mg/liter. Also, sodium carbonate etc. of 1.1 to 1.2 equivalents of the quantity of chlorine contained in the plastic waste were continuously supplied into the tank 2.

[0038] As the oilification apparatus 4, an electric furnace formed by dividing a reaction tube into three was used. The reaction tube, which measured 5 mm in inside diameter, 10 mm in outside diameter, and 60mm in length, and was made of SUS316, was subjected to anticorrosion treatment before the use thereof by circulating 1% aqueous sodium carbonate for 50 hours in a state in which it had been heated in advance to the oilification condition of plastic waste. By forming corrosion preventive film on the inside surface of the reaction tube in this manner, corrosion due to sodium chloride caused by neutralization can be prevented more effectively.

[0039] The temperature in the oilification apparatus was adjusted so as to be 20 to 250°C at the preheating portion, 250 to 350°C at the subcritical portion, and 350 to 550°C at the supercritical portion, and the pressure therein was adjusted so as to be 250 to 300 kgf/cm² (25 to 30 MPa).

[0040] Each kind of plastic waste was treated under the conditions of working examples 1 and 2 given in Table 1, and in both cases, corrosion was not observed at all on the inside surface of the reaction tube and the equipments after the operation for 2000 hours. The results are given in Table 1

Table 1

Condition	Working example1	Working example2	Working example3	Working example4	Working example5	Working example6
Quantity of plastic waste (kg/h)	0.3	0.3	0.5	1.2	1.2	1.2
Composition of plastic waste (wt%)						
Vinyl chloride resin	100	100	50	50	50	30
Polystyrene	0	0	50	50	50	30
Polystyrene	0	0	0	50	0	30
Concentration of plastic in slurry (wt%)	16.7	16.7	25.0	25.0	25.0	25.0
Decolorization method	N ₂ blowing	N ₂ blowing /decolorizer	N ₂ blowing /decolorizer	N ₂ blowing /decolorizer	N ₂ blowing /decolorizer	N ₂ blowing /decolorizer
Kind of decolorizer	-	Na ₂ SO ₃	Na ₂ SO ₃	Na ₂ SO ₃	Na ₂ SO ₃	Na ₂ SO ₃
Dissolved oxygen concentration (mg/l)	0.5	0.2	0.1	0.2	0.2	0.3
Kind of salt	Na ₂ CO ₃	Na ₂ CO ₃	CaCO ₃	Mg(OH) ₂	Ca(OH) ₂	Na ₂ CO ₃
Amount of addition of salt Equivalent ratio to decolorization amount	1.2	1.1	1.1	1.1	1.1	1.1
Subcritical condition						
Temperature (°C)	330	330	330	330	350	350
Time (min)	30	30	30	30	30	20
Supercritical condition						
Temperature (°C)	480	480	480	480	500	500
Pressure (kg/cm ²)	300	300	300	300	300	300
Time (min)	5	5	5	5	2	2
Yield (wt%)						
Gas content	21	19	15	13	17	12
Oil content	35	36	62	64	61	73
Operation time (h)	2000	2000	100	100	100	100
Corrosion condition (mm/year)	No abnormality 0.1 or less	No abnormality 0.1 or less	No abnormality 0.1 or less	No abnormality 0.1 or less	No abnormality 0.1 or less	No abnormality 0.1 or less

[0041] The above is an explanation of the embodiment and the working examples of the present invention. These are described to facilitate the understanding of the present invention, and do not limit the scope of the present invention. All changes, modifications, and additions obvious to persons skilled in the art of the invention defined in claims are

embraced in the technical scope of the present invention.

[0042] For example, in the explanation of the embodiment with reference to the above figures, continuous treatment has been carried out by making the mixed liquid in a flowable slurry form. However, the present invention is not limited to this treatment process.

- 5 [0043] Further, for example, batch treatment may be carried out in which a mixed liquid of plastic waste and aqueous solution is put into a container and is heated, and thereafter the treatment condition is transferred to supercritical condition.

INDUSTRIAL APPLICABILITY

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[0044] According to the oilification process for chlorine-based plastic waste in accordance with the present invention, compared with the prior art, the treatment process and apparatus can be simplified significantly, and also even if an inexpensive apparatus is used, corrosion does not occur in the apparatus.

- 15 [0045] All of the claims, specification, drawings, and abstract of Japanese Patent Application No. 10-192859 (No. 192859/1998) filed on July 8 in 1998 and a part of description of the specification thereof are quoted in this description.

Claims

- 20 1. An oilification process for chlorine-based plastic waste characterized in that a mixture of plastic waste including chlorine-based plastic and an aqueous solution containing carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal or several kinds of these compounds, in which the concentration of dissolved oxygen is controlled so as to be not higher than 0.5 mg/liter, is heated; chlorine in said plastic waste is released during a process of transfer to a supercritical condition and/or under a supercritical condition; and said plastic waste is decomposed.
- 25 2. An oilification process for chlorine-based plastic waste characterized in that an aqueous solution containing carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal or several kinds of these compounds is heated; melted plastic waste including chlorine-based plastic is mixed in said aqueous solution during a process of transfer to a supercritical condition and/or under a supercritical condition; the concentration of dissolved oxygen in said aqueous solution is controlled so as to be not higher than 0.5 mg/liter before or during the mixing of said plastic waste; chlorine in said plastic waste mixed in said aqueous solution is released; and said plastic waste is decomposed.
- 30 3. The oilification process for chlorine-based plastic waste according to claim 1 or 2, wherein chlorine released from said plastic waste is neutralized by carbonate of an alkali metal or hydroxide or carbonate of an alkali earth metal.
- 35 4. The oilification process for chlorine-based plastic waste according to claim 1 or 2, wherein means for controlling the concentration of dissolved oxygen is blowing of nitrogen gas or addition of a deoxidizer.
- 40 5. The oilification process for chlorine-based plastic waste according to claim 4, wherein said deoxidizer is sodium sulfite, sodium nitrite, or hydrazine.

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FIG. 1

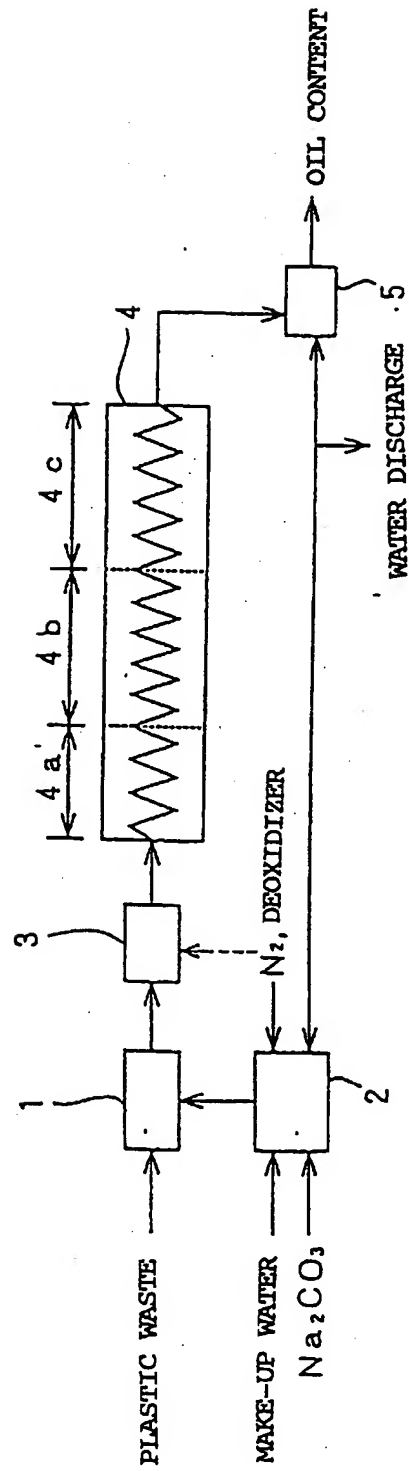
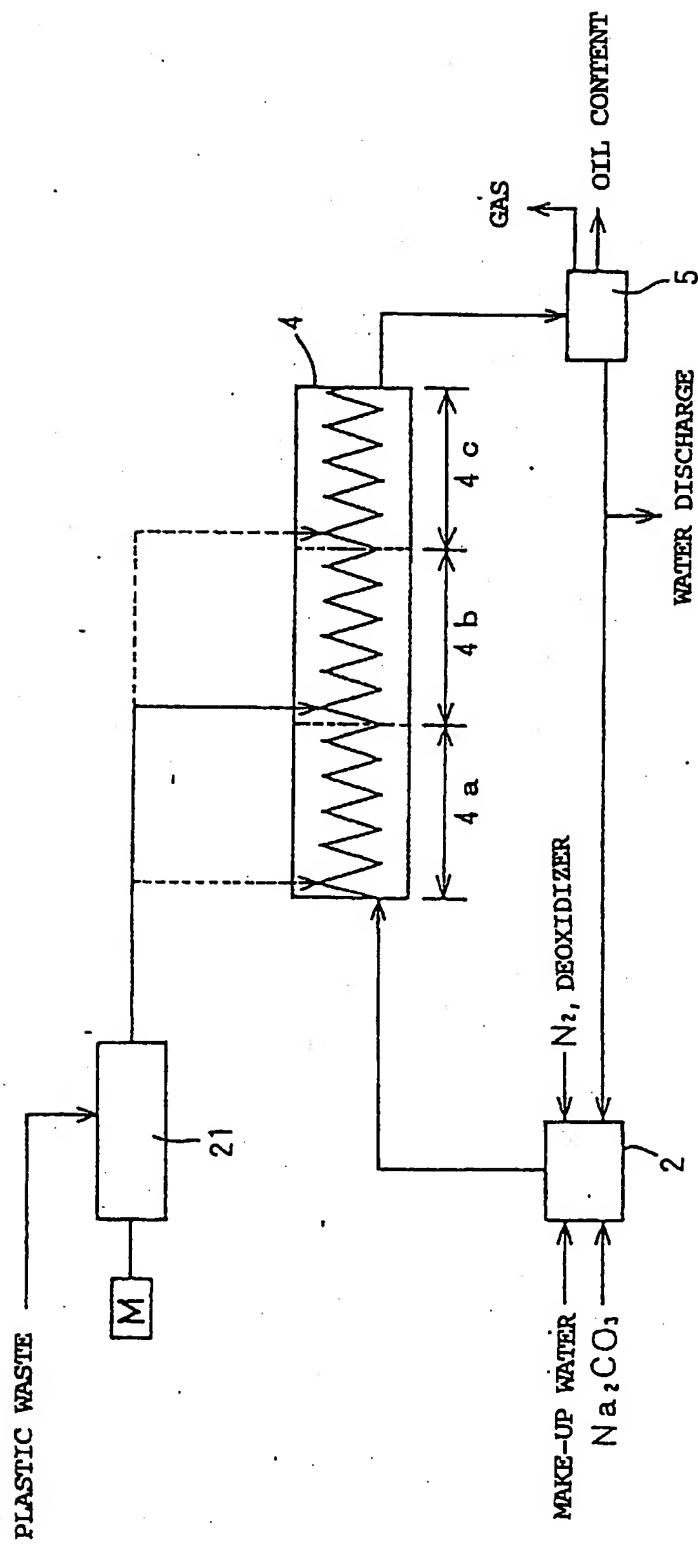


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/03612

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ C10G1/10, C10J3/46, B09B3/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ C10G1/10, C10J3/46, B09B3/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 10-88146, A (Kaneka Corp.), 7 April, 1998 (07. 04. 98) (Family: none)	1-5
Y	JP, 10-8065, A (Nishikawa Rubber Co., Ltd.), 13 January, 1998 (13. 01. 98)	1-5
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 28 July, 1999 (28. 07. 99)		Date of mailing of the international search report 10 August, 1999 (10. 08. 99)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)